MICROENCAPSULATION OF POLYFUNCTIONAL AMINES FOR SELF-HEALING OF EPOXY-BASED COMPOSITES

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Introduction

Epoxy-based composites have wide application everywhere from consumer goods to aerospace applications. Once damaged, however, the composite loses a great deal of strength. The addition of self-healing functionality to an epoxy composite enables the repair of damage caused by fatigue or tensile fracture and the potential for extended service life.

Prior work on self-healing epoxies in our group has focused on a ring-opening metathesis polymerization to form a crosslinked film of polydicyclopentadiene (DCPD) to arrest crack growth and re-bond the material, and has demonstrated up to a 90% recovery in fracture toughness[1-4]. However, the materials for this reaction are costly and can be air and moisture sensitive.

We discuss here the preparation of microcapsules containing an amine hardener (DEH-52, Dow Chemical) for use as the hardener in a 2-part epoxy healing system consisting of epoxy-containing capsules and hardener-containing capsules. Similar polyamine-based capsules have been reported in the literature for catalyst storage and isolation[5,6]. The system employed is an emulsion of two immiscible solvent phases with monomers dissolved to perform an interfacial polymerization between an isocyanate and a polyamine to form a polyurea shell while leaving sufficient polyamine in the core to serve as a curing agent for an epoxy, specifically Epon 828 resin. Span 85 was selected as a surfactant due to its ability to stabilize water-in-oil emulsions[7].

Experimental

Materials. Isophorone diisocyanate (IPDI) was used as received from Bayer. DEH-52 was used as received from Dow Chemical. Acetonitrile, methanol, cyclohexane, adipoyl chloride, and Span 85 were used as received from Sigma-Aldrich.

Instrumentation. An overhead stand mixer (Caframo BDC6015) with three-bladed hydrofoil impeller was used to prepare the emulsions. Optical imaging was performed using a QImaging Micropublisher camera on a Leica microscope. Scanning electron microscopy was performed on a Philips XL30 ESEM-FEG instrument.

Microencapsulation Procedure. 10 g of a 2:1 v/v mixture of DEH-52 and diluent solvent, either methanol or acetonitrile. was added to a 100 mL solution of 5% w/v of Span 85 in cyclohexane The mixture was stirred in an ice water bath for 10 minutes at 1000 RPM to emulsify. To this emulsion was added 0.67 g of IPDI in 10 g cyclohexane. Optionally, 0.67 g of adipoyl chloride in 10 g cyclohexane was also added. Interfacial polymerization began immediately and was substantially complete within 5 minutes. Stirring was continued for 2 hours, after which the capsules formed were allowed to settle and excess solvent was decanted. The capsules were then washed 5 times with DI water and dried by filtration.

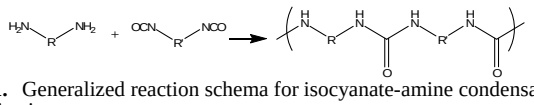


Figure 1. Generalized reaction schema for isocyanate-amine condensation polymerization.

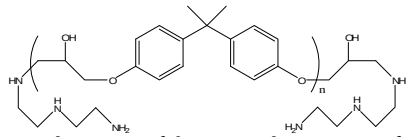


Figure 2. Chemical structure of the principal component of DEH-52, a diethylenetriamine (DETA) adduct of DGEBA. The other component is excess DETA.

Results and Discussion

Isophorone Diisocyanate-Walled DEH-52 Capsules. Upon emulsification of the DEH-52/solvent phase in cyclohexane, the solution appeared cloudy but colorless. Aliquots taken of this mixture showed a propensity for the suspended phase to readily recombine, indicating that the emulsion as prepared was not entirely stable. Following the bolus addition of IPDI, white particles were evident – the microcapsules – and recombination of the suspended phase was impossible. Filtration of the capsules proceeded without incident and capsules were removed for examination by optical and scanning electron microscopy. Optical images of the capsules suggested a thick wall; this observation was confirmed by SEM. Since the wall material was formed primarily by interfacial polymerization, it was a surprise to see that the wall appeared quite porous (Figure 3a). Further investigation revealed the wall was formed as a sticky aggregate of smaller polymer droplets (Figure 3b) rather than a continuous film of polymer. We suggest that this particular wall microstructure is due to a limited solubility of oligomer in opposing phase and subsequent reaction and entanglement to form solid nanospheres, which then aggregate at the interface to form a wall. These microcapsules were brittle and could not be dispersed in an epoxy resin without fracture. Subsequently, a toughening agent (adipoyl chloride) was added during the initial encapsulation phase to produce a polyamide membrane over the polyurea shell.

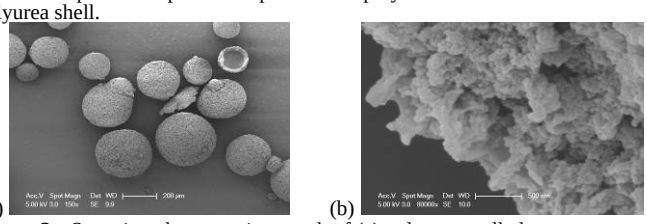


Figure 3. Scanning electron micrograph of (a) polyurea-walled microcapsules prepared by interfacial polymerization with IPDI. (b) Higher magnification image of the shell wall material.

Isophorone Diisocyanate and Adipoyl Chloride-Walled DEH-52 Capsules. A second batch of microcapsules was prepared by addition of two wall-forming agents: the diisocyanate previously discussed, and adipoyl chloride, a diacid chloride. The diacid chloride was chosen in order to form a polyamide film around the extant capsule wall to retain core material. The diisocyanate was added as before, and allowed to react for 1 minute prior to addition of the diacid chloride. Following addition of the diacid chloride, the mixture became slightly more viscous and briefly turned a pink color before fading back to an off-white. The reason for this color change is not entirely understood. The capsules were isolated as discussed above and micrographed. The capsules prepared with diacid chloride exhibited a different shape from those without. This batch of capsules appeared shriveled as a result of the diacid chloride addition (Figure 4). This is likely the result of additional core material continuing to react with the acid chloride and the abstraction of diluting solvent from the core by the acid chloride. Both result in wall thickening at the cost of core fill content.

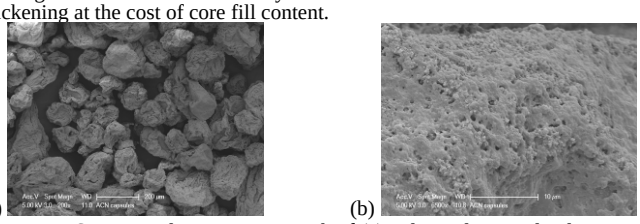
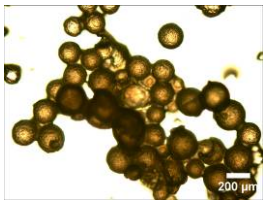


Figure 4. Scanning electron micrograph of (a) polyamide coated polyurea microcapsules. (b) Close-up view of wall showing enhanced coating integrity.

Fill Content Analysis. Microcapsules from the isocyanate-only synthesis were deposited on a glass slide for a crush test. The capsules were allowed to dry, were sandwiched below another glass slide, and then were imaged before and after applying pressure intended to rupture the capsule walls (Figure 5). Ample fluid was released during this test. A single drop of Epon 828 resin was added to the fluid between the slides and manually mixed. The material was allowed to cure at 35 °C for 2 days. Following the cure cycle, a toughened film of cured epoxy was observed between the slides. While it is unlikely that the stoichiometry of the epoxide resin to the encapsulated curing agent was ideal, the presence of a cured film suggests that curing agent was present in the capsules and was readily released upon crushing of the capsular walls.

When a similar test was performed on the acid chloride-treated microcapsules, minimal fluid was released. This fluid was also unsuccessful at curing epoxy at 35 °C for 7 days. However, when a similar sample was heated to 85 °C for 3 hours and let cool for 1 day, a cured film formed, suggesting the presence of curing agent in the capsule.

Thermal Analysis. Thermogravimetric analysis was performed on both the DEH-52 and the capsules prepared by isocyanate reaction. DEH-52 shows a sharp mass loss corresponding to DETA at 185 °C, followed by a complete decomposition at 400 °C. The capsules prepared show a slightly earlier decomposition, and a slightly later DETA release as well as bound water or solvent in the shell wall (Figure 6).

(a) 

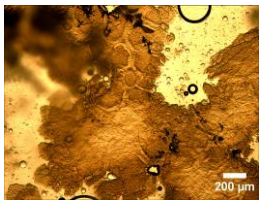
(b) 

Figure 5. Optical micrograph of filled capsules (a) prior to crushing and (b) after crushing.

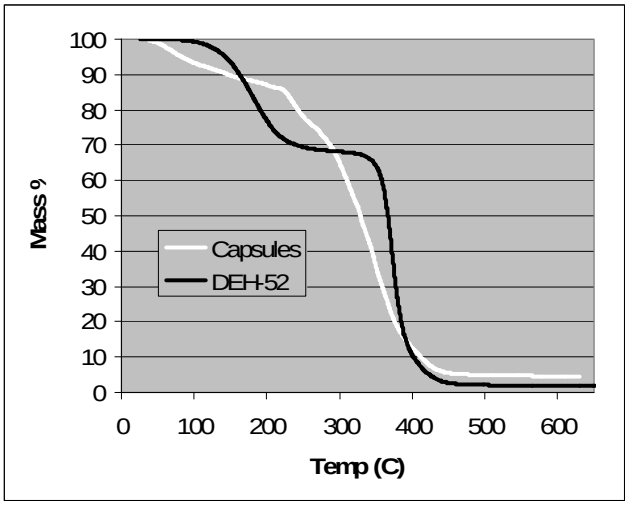


Figure 6. Thermogravimetric analysis comparing capsule content to DEH-52.

Conclusions

We have demonstrated the successful encapsulation, release, and hardening behavior of a polyamine intended as a curing agent in a two-part epoxy. The polyamine used is water-soluble and forms a semistable emulsion in cyclohexane when a surfactant with low hydrophilic-lipophilic ratio is used. Because this healing chemistry is epoxy-based, it is more compatible with an epoxy matrix material, and it is less sensitive to air, moisture, and light than the Grubbs' catalyst-dicyclopentadiene system currently employed.

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